

Electronic Supplementary Information

Metalloporphyrin-Bound Janus Nanocomposites with Dual Stimuli Responsiveness for Nanocatalysis in Living Radical Polymerization

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Experiment Section

Materials

The following chemicals were purchased from commercial suppliers (Sigma-Aldrich or Alfa Aesar) and used as received without further purification, unless otherwise noted: benzaldehyde ($\geq 99.5\%$), 4-hydroxybenzaldehyde (98%), pyrrole ($\geq 98\%$), propionic acid ($\geq 99.5\%$), propargyl bromide (80 wt% in toluene), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 95%), polyoxyethylene (5) nonylphenylether (Igepal CO-520), 1-octadecene (90%), oleic acid (90%), [3-(2-aminoethylamino)propyl]trimethoxysilane (APMS, 97%), tetraethyl orthosilicate (TEOS, 98%), (3-chloropropyl)triethoxysilane (CPES, 95%), ammonium hydroxide solution (28.0~30.0 wt% NH_3 basis), sodium azide (NaN_3 , $\geq 99.5\%$) and *N,N,N',N',N''*-pentamethyl diethylene triamine (PMDETA, 99%). The liquid monomers, methyl acrylate (MA, 99%), *n*-butyl acrylate (*n*BA, $\geq 99\%$), glycidyl methacrylate (GMA, $\geq 97\%$), *N*-(2-hydroxypropyl) methacrylate (HPMA, 99%) and styrene (St, $\geq 99\%$) were purified by percolating over an inhibitor-removal column. *N*-isopropylacrylamide (NIPAM, 97%) was recrystallized twice from toluene/hexane (7:3, v/v).

Synthesis of 5-(4'-Hydroxyphenyl)-10,15,20-triphenylporphyrin (TPP-OH)

5-(4'-Hydroxyphenyl)-10,15,20-triphenylporphyrin (TPP-OH) was prepared according to the method reported in literature with slight modification.¹⁻³ Benzaldehyde (**2**, 5.48 mL, 54 mmol), 4-hydroxybenzaldehyde (**3**, 2.20 g, 18 mmol) and propionic acid (240 mL) were introduced into a three-necked round-bottomed flask fitted with a condenser. The flask was allowed to proceed at 135 °C for 1 h. Then freshly distilled pyrrole (**1**, 5.00 mL, 72 mmol) was added dropwise to the solution under argon atmosphere. Upon completion of the addition, the reaction mixture was refluxed for another 1 h. The solvent was

removed under reduced pressure and the residue was diluted with methanol (200 mL). A purple precipitate was collected by filtration after the solution being stored at 0 °C overnight. The crude product was purified by column chromatography on silica gel eluting with chloroform: methanol (95:5, v/v) to give compound **4** as a purple solid. Yield: 4.9%. ¹H NMR (400 MHz, CDCl₃, ppm): 8.86 (m, 8H, β-pyrrole), 8.21 (m, 6H, 10, 15, 20-Ar-*o*-H), 8.04 (m, 2H, 5-Ar-*o*-H), 7.75 (m, 9H, 10, 15, 20-Ar-*m*- and *p*-H), 7.16 (m, 2H, 5-Ar-*m*-H), -2.74 (s, 2H, -NH-). ESI-MS (*m/z*): 630.7, calculated for [C₄₄H₃₀ON₄]⁺: 630.7. UV-vis (CHCl₃) λ_{max} nm (ε, 10⁻³ L mol⁻¹cm⁻¹): 419, 518, 556, 598, 648.

Synthesis of 5-(4'-Propargyloxyphenyl)-10,15,20-triphenylporphyrin (PTPP)

In a typical procedure, TPP-OH (**4**, 0.63 g, 1 mmol), propargyl bromide (2.23 mL, 20 mmol, 80 wt% in toluene), K₂CO₃ (2.8 g, 20 mmol) and anhydrous DMF (100 mL) introduced into a round-bottomed flask. The solution was stirred in dark at room temperature under argon atmosphere for 24 h. After solvent removal, the crude product was redissolved in CH₂Cl₂, washed with water thrice, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel eluting with dichloromethane to give compound **5** as a purple solid. Yield: 94%. ¹H NMR (400 MHz, CDCl₃, ppm): 8.86 (m, 8H, β-pyrrole), 8.22 (m, 6H, 10, 15, 20-Ar-*o*-H), 8.04 (m, 2H, 5-Ar-*o*-H), 7.76 (m, 9H, 10, 15, 20-Ar-*m*- and *p*-H), 7.16 (m, 2H, 5-Ar-*m*-H), 4.96 (t, 2H, -OCH₂C≡CH), 2.68 (t, 1H, -C≡CH), -2.74 (s, 2H, -NH-). ESI-MS (*m/z*): 668.7, calculated for [C₄₇H₃₂ON₄]⁺: 668.7. UV-vis (CHCl₃) λ_{max} nm (ε, 10⁻³ L mol⁻¹cm⁻¹): 418, 518, 556, 597, 648.

Synthesis of 5-(4'-Propargyloxyphenyl)-10,15,20-triphenyl-21*H*,23*H*-porphine Zinc (ZnPTPP)

5-(4'-Propargyloxyphenyl)-10,15,20-triphenyl-21*H*,23*H*-porphine zinc (ZnPTPP) was synthesized by metalation of PTPP with zinc acetate. PTPP (**5**, 0.67 g, 1 mmol) and zinc(II) acetate (1.84 g, 10 mmol) were dissolved in a mix solution of CHCl₃/CH₃OH (1:1, v/v). The reaction mixture was allowed to proceed at room temperature for 12 h. After solvent removal, the crude product was redissolved in CH₂Cl₂, washed with water thrice, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel eluting with chloroform: hexane (90:10, v/v) to give compound **6** as a purple solid. Yield: 92%. ¹H NMR (400 MHz, CDCl₃, ppm): 8.94 (m, 8H, β-pyrrole), 8.22 (m, 6H, 10, 15, 20-Ar-*o*-H), 8.13 (m, 2H, 5-Ar-*o*-H), 7.76 (m, 9H, 10, 15, 20-Ar-*m*- and *p*-H), 7.35 (m, 2H, 5-Ar-*m*-H), 4.96 (t, 2H, -OCH₂C≡CH), 2.68 (t, 1H, -C≡CH). ESI-MS (*m/z*): 732.2, calculated for [C₄₇H₃₀ON₄Zn]⁺: 732.1. UV-vis (CHCl₃) λ_{max} nm (ε, 10⁻³ L mol⁻¹cm⁻¹): 418, 518, 552, 595, 648.

Synthesis of Fe₃O₄@*a*SiO₂-N₃ Janus Nanoparticles

Monodisperse oleic acid-capped Fe₃O₄ nanoparticles with a mean diameter of ~12 nm were prepared as described in literature by Part et al.^{4,5} In a typical synthetic procedure, 6 mL of aqueous solution of FeCl₃•6H₂O (541 mg, 2 mmol) were dosed to a mixed solution of oleic acid (1.9 mL, 6 mmol), ethanol (8 mL) and hexane (14 mL) under vigorous stirring for 0.5 h. Afterward, NaOH (160 mg, 4 mmol) was added to the above solution and the reaction was allowed to proceed at 70 °C for 4 h. After being cooled down to ambient temperature, the organic phase was collected and purified by repeated washing with deionized water. Most of solvents were removed under reduced pressure. The highly viscous iron/oleate complex precursor was redispersed in a mixed solution of oleic acid

(0.32 mL, 1 mmol) and 1-octadecene (12.5 mL, 40 mmol), sonicated for 0.5 h and degassed by bubbling nitrogen for 0.5 h. The reaction then was allowed to proceed at 320 °C for 0.5 h under steady and continuous nitrogen flow. After being cooled down to room temperature, the crude product was purified by repeated precipitation from hexane into excessive ethanol. The oleic acid-stabilized Fe₃O₄ nanoparticles were centrifuged and stored in cyclohexane before use.

The heteroepitaxial deposition of silica frameworks on the Fe₃O₄ nanoparticles were conducted using a reverse microemulsion method.⁶⁻⁸ Typically, the as-prepared Fe₃O₄ nanoparticles in cyclohexane (5.0 mL, 2.5 mg/mL) was dispersed in a mixed solution containing Igepal CO-520 (5.0 g), cyclohexane (120 mL) and ammonium hydroxide solution (2.0 mL, 28~30 wt% NH₃ basis) under ultrasonication treatment. Afterward, TEOS (0.1 mL) and APMS (0.1 mL) was dropwise introduced to the reaction suspension in 0.5 h. The rest of TEOS (0.1 mL × 3) and CPES (0.3 mL × 1) was dosed to the reaction mixture at a time interval of 12 h. Finally, the raw product was collected with a magnet, and purified by three cycles of centrifugation/redispersion/washing in excessive ethanol. The Fe₃O₄@SiO₂ heteronanoparticles were centrifuged and stored in ethanol before use.

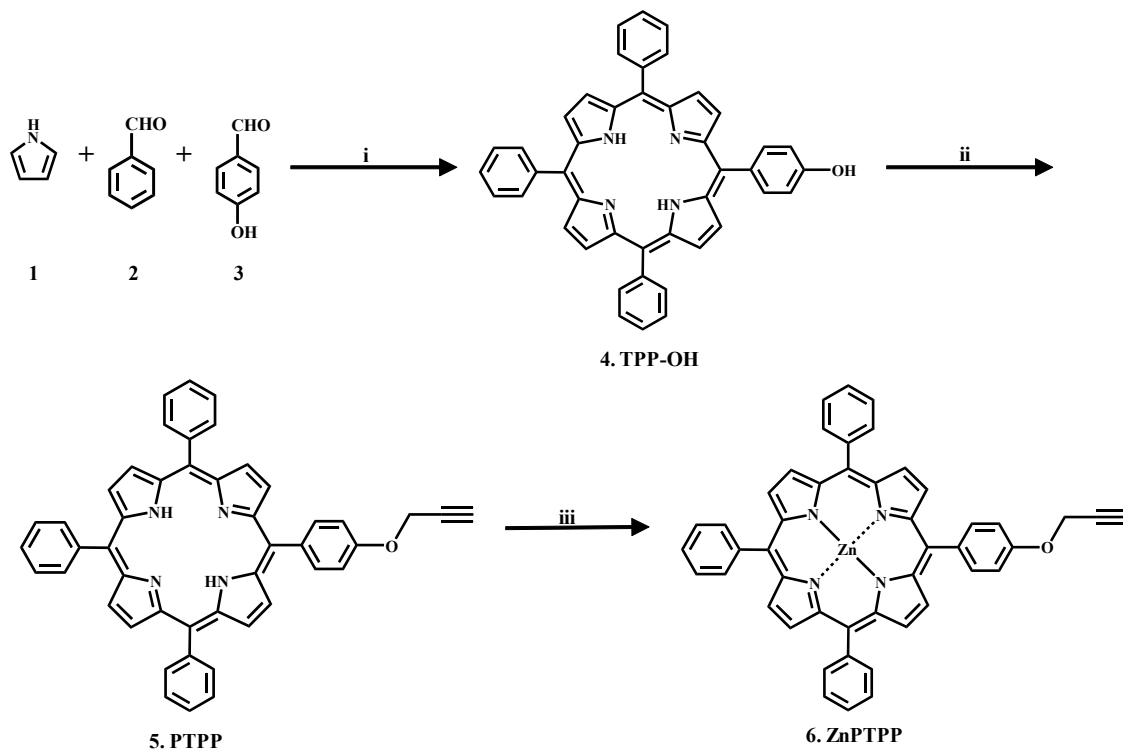
To synthesize Fe₃O₄@SiO₂-N₃ Janus nanoparticles, about 40 mg of Fe₃O₄@SiO₂ Janus nanoparticles was dispersed into an ethanol and deionized water (10 mL: 10 mL) mixture by ultrasonication for 0.5 h. NaN₃ (50 mg) was added to the reaction mixture. The reaction was allowed to proceed at 50 °C for 4 h under vigorous stirring. After the

reaction, the purification of $\text{Fe}_3\text{O}_4@ \text{aSiO}_2\text{-N}_3$ Janus nanoparticles was done by three cycles of centrifugation/redispersion/washing in a mixed solution of ethanol and deionized water (1:1, v/v). The $\text{Fe}_3\text{O}_4@ \text{aSiO}_2\text{-N}_3$ Janus nanoparticles were centrifuged and stored in ethanol before use.

Instrumentation

^1H NMR spectroscopy were carried out with Bruker ARX 400 MHz NMR spectrometer with chemical shifts reported in ppm using solvent residue as the internal reference. UV-vis absorption spectra were acquired on a Hitachi U-3010 UV-vis photospectrometer equipped with a temperature controller. Fourier transform infrared spectroscopy (FTIR) analysis was detected by a Bio-Rad FTS 135 Fourier transform infrared spectrophotometer, and the diffuse reflectance spectra were scanned within the range from 4000 to 400 cm^{-1} . The thermal stability of the polymers and nanoparticles was investigated by thermogravimetric analysis (TGA). The samples were heated from 25 °C to around 800 °C with a heating rate of 10 °C/min under a dry nitrogen atmosphere in a Shimadzu DTG-60AH TGA-DTA Analyzer. Transmission electron microscopy (TEM) measurements were conducted on a JEOL JEM-2100F microscope operated at 200 kV. Surface compositions of the nanoparticles were detected by X-ray photoelectron spectroscopy (XPS) measurements on a Kratos AXIS Ultra DLD spectrometer sourcing with a monochromatized Al $K\alpha$ X-ray source (1468.71 eV photons). ^1H NMR spectroscopy were carried out with Bruker ARX 400 MHz NMR spectrometer with chemical shifts reported in ppm using solvent residue as the internal reference. Gel permeation chromatography (GPC) measurements were monitored with an Agilent 1260 system using THF as the eluent at a flow rate of 1.0 mL/min. A refractive index detector,

5 μm guard column, three PL gel columns (two Agilent Mixed-C 5 μm columns and one Agilent Mixed-D 5 μm column) and narrow poly(methyl methacrylate) (PMMA) molecular weight standards were used.



Scheme S1. Reagents and conditions: (i) propionic acid, 135 °C, 4 h; (ii) propargyl bromide, K_2CO_3 , anhydrous DMF, Ar, RT, 24 h; (iii) Zn(II) acetate, $CHCl_3/CH_3OH$, RT, 12 h.

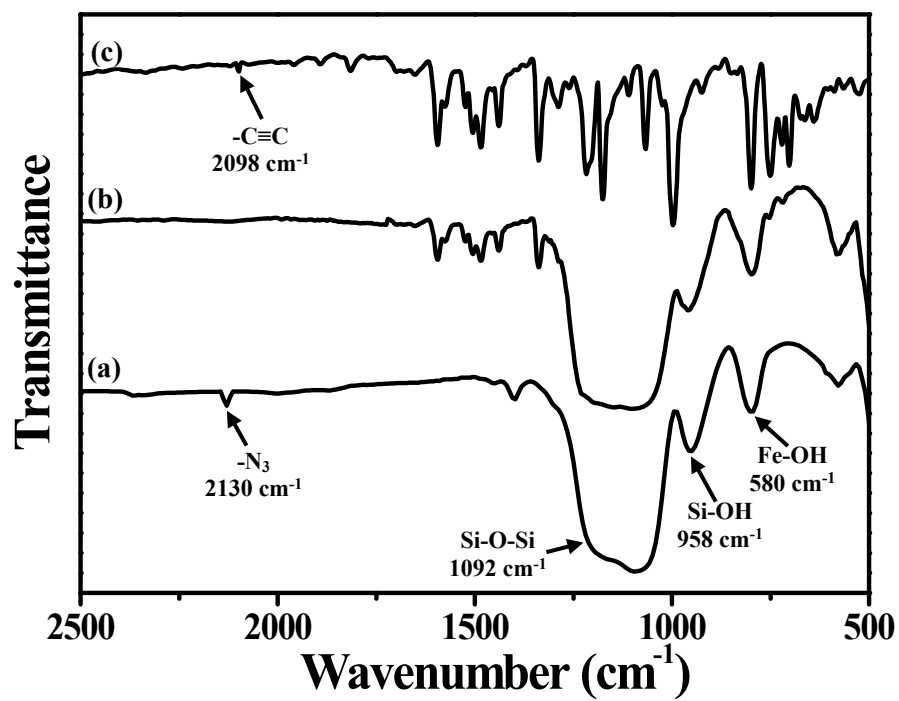


Figure S1. FTIR spectra of the (a) Fe₃O₄@aSiO₂-N₃, (b) Fe₃O₄@aSiO₂-click-ZnPTTP nanoparticles and (c) ZnPTTP.

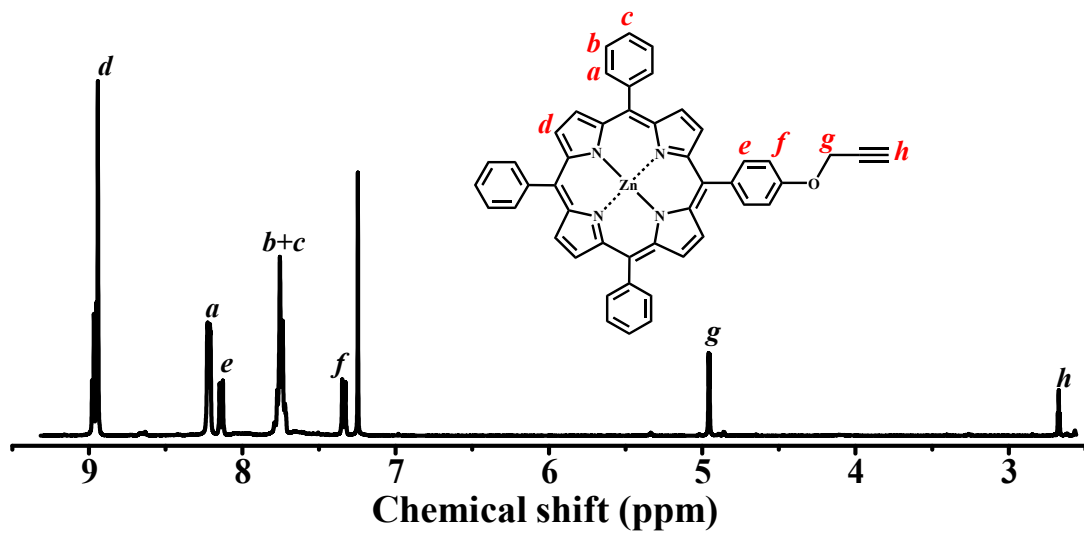


Figure S2. ¹H NMR spectrum of the ZnPTPP in CDCl₃.

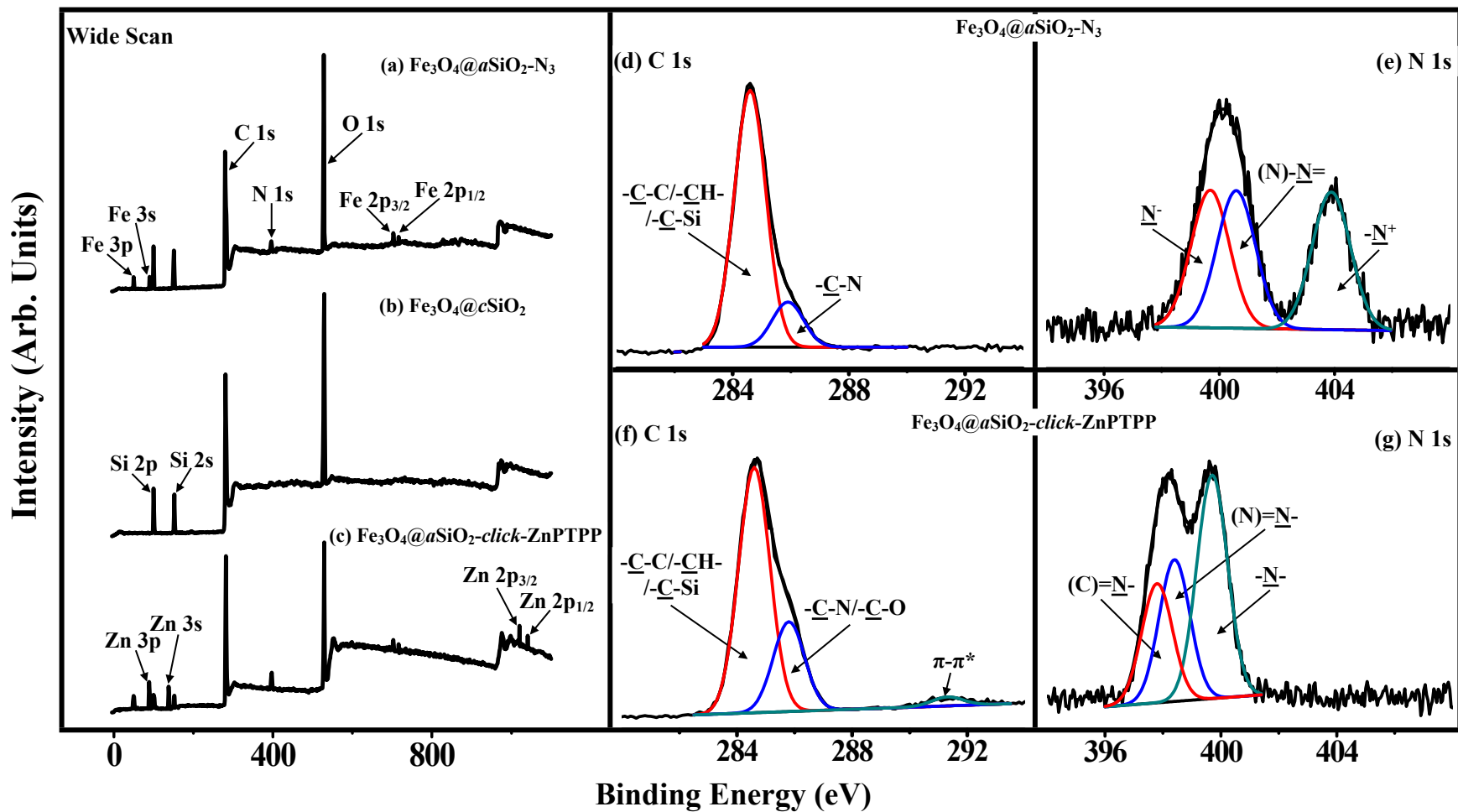


Figure S3. XPS wide-scan, C 1s and N 1s core-level spectra of the (a,d,e) Fe₃O₄@aSiO₂-N₃, (b) Fe₃O₄@cSiO₂ and (c,f,g) Fe₃O₄@aSiO₂-click-ZnPTTP nanoparticles.

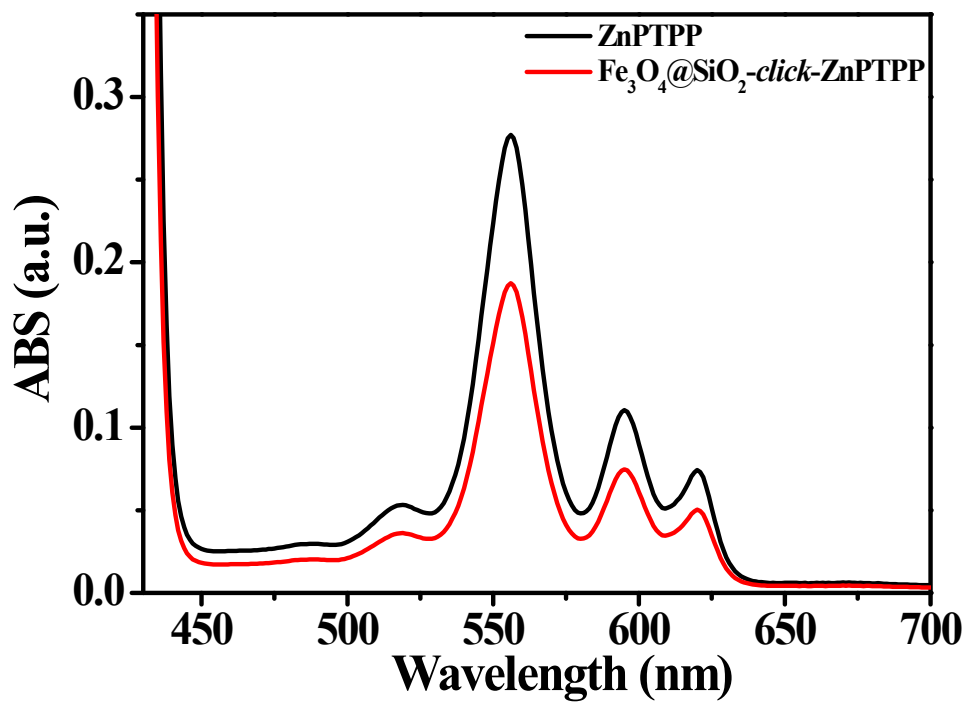


Figure S4. UV-vis absorption spectrum of ZnPTPP precursor and Fe₃O₄@aSiO₂-click-ZnPTPP Janus nanocomposites dispersed in DMSO. UV-vis (DMSO) λ_{max} nm (ϵ , 10^{-3} L mol⁻¹cm⁻¹): 418, 518, 552, 595, 648.

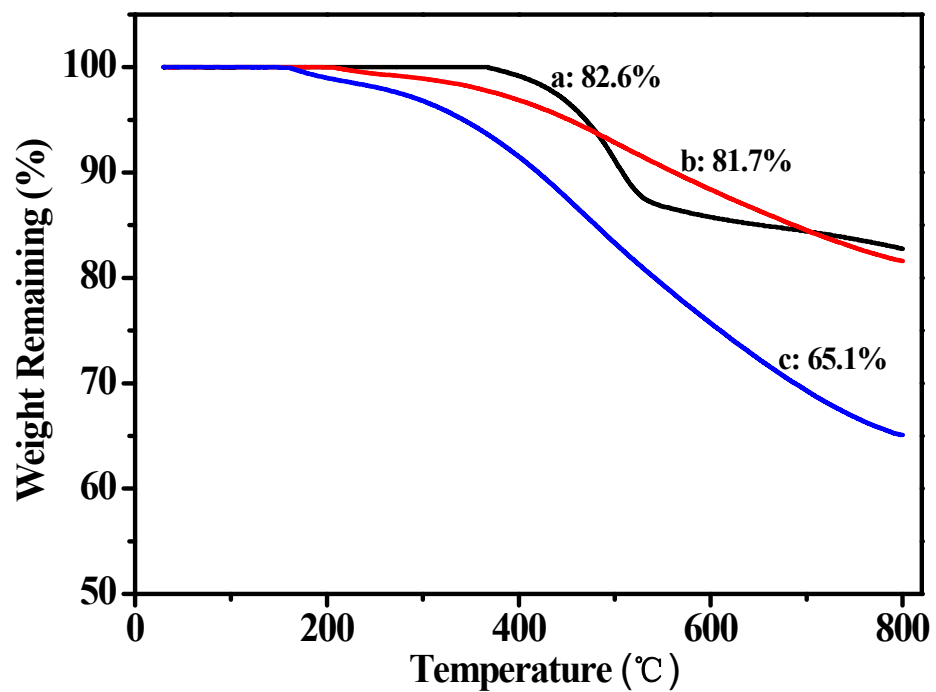


Figure S5. TGA curves of the (a) $\text{Fe}_3\text{O}_4@a\text{SiO}_2\text{-N}_3$, (b) $\text{Fe}_3\text{O}_4@a\text{SiO}_2\text{-click-ZnPTTP}$ nanoparticles and (c) ZnPTTP.

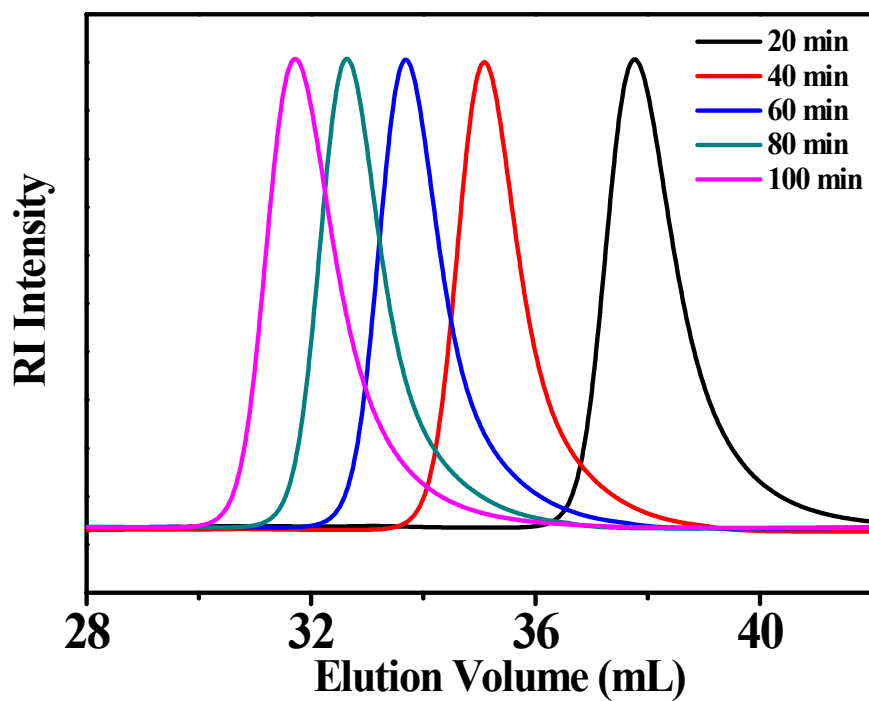


Figure S6. Molecular weight distributions at different time points of PET-RAFT polymerization of MA with 10 ppm $\text{Fe}_3\text{O}_4@a\text{SiO}_2\text{-click-ZnPTTP}$ hybrid nanocatalysts in DMSO in the absence of oxygen at 25 °C under green LED light irradiation (5 W, $\lambda_{\text{max}} = 520$ nm, 1.3 mW/cm²) with DDMAT as the CTA ([MA]/[DDMAT] = 200:1).

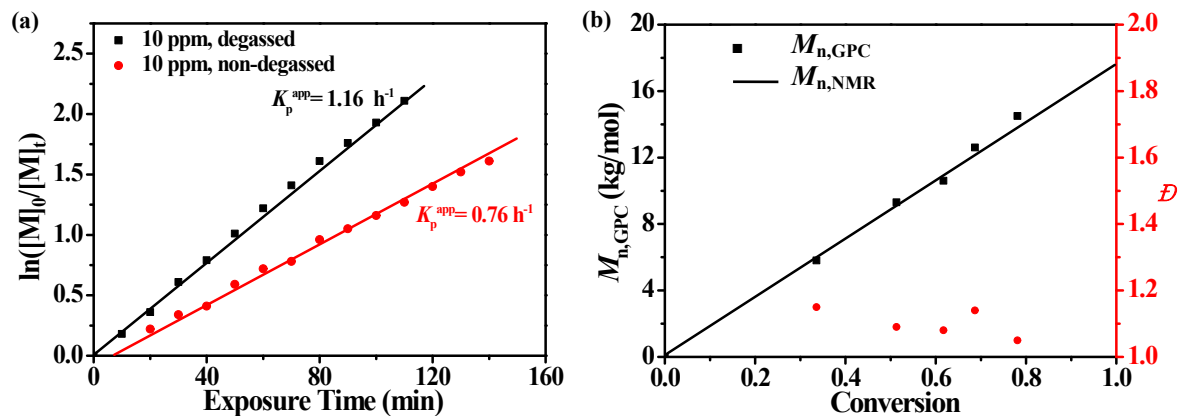


Figure S7. Kinetic analysis of PET-RAFT polymerization of MA with 10 ppm $\text{Fe}_3\text{O}_4@a\text{SiO}_2\text{-click-ZnPTTP}$ hybrid nanocatalysts in DMSO with and without deoxygenation at 25 °C under green LED light irradiation (5 W, $\lambda_{\text{max}} = 520 \text{ nm}$, 1.3 mW/cm^2) with DDMAT as the CTA ($[\text{MA}]/[\text{DDMAT}] = 200:1$). (a) Plot of $\ln([M]_0/[M]_t)$ versus exposure time t in reference to monomer concentration; and (b) $M_{n,NMR}$, $M_{n,GPC}$ and \bar{D} versus monomer conversion.

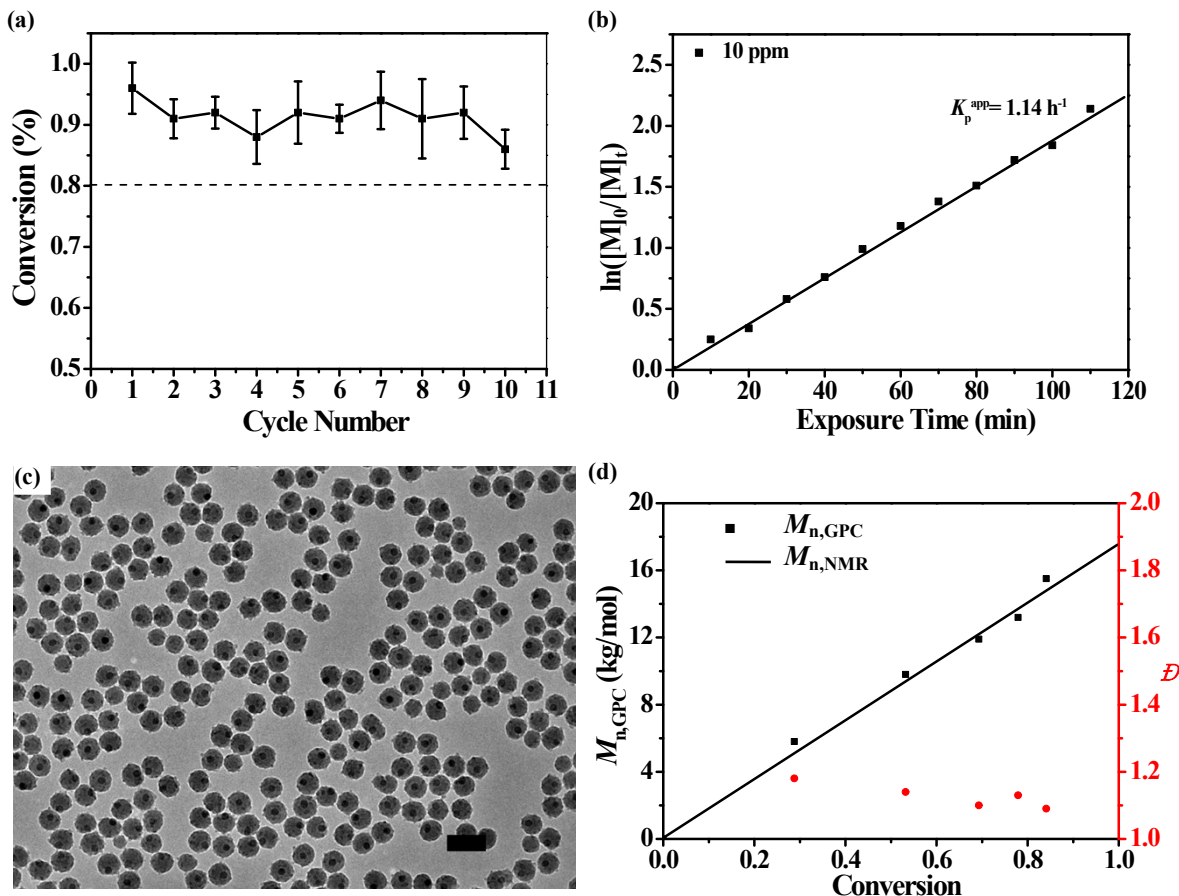


Figure S8. Polymerization of MA using 10 ppm $\text{Fe}_3\text{O}_4@ \text{aSiO}_2\text{-click-ZnPTTP}$ hybrid nanocatalysts in DMSO in the absence of oxygen at 25 °C under green LED light irradiation (5 W, $\lambda_{\text{max}} = 520 \text{ nm}$, 1.3 mW/cm^2) with DDMAT as the CTA ($[\text{MA}]/[\text{DDMAT}] = 200:1$). (a) The average polymerization yields of PMA; (b) plot of $\ln([M]_0/[M]_t)$ versus exposure time t ; (c) TEM image of $\text{Fe}_3\text{O}_4@ \text{aSiO}_2\text{-click-ZnPTTP}$ hybrid nanocatalysts (the scale bar is 50 nm); and (d) $M_{n,\text{NMR}}$, $M_{n,\text{GPC}}$ and D versus monomer conversion after ten successive polymerization and reuse of the involved nanocatalysts by centrifugation.

Table S1. PET-RAFT Polymerization of Different Monomers Using Fe₃O₄@aSiO₂-click-ZnPTPP Janus Nanocomposites as Photocatalysts

Entry	Photocatalyst	Monomer	CTA	[PC]/[M] ^a (ppm)	time (h)	α^b (%)	$M_{n,NMR}^b$ (kg/mol)	$M_{n,GPC}^c$ (kg/mol)	\mathcal{D}^c
1 ^d	Fe ₃ O ₄ @aSiO ₂ -click-ZnPTPP	MA	CPPA	10	12	15	2.9	3.2	1.13
2	Fe ₃ O ₄ @aSiO ₂ -click-ZnPTPP	MA	CPPA	50	12	22	4.2	4.4	1.09
3	Fe ₃ O ₄ @aSiO ₂ -click-ZnPTPP	St	DDMAT	10	12	55	11.8	14.2	1.18
4	Fe ₃ O ₄ @aSiO ₂ -click-ZnPTPP	<i>n</i> BA	DDMAT	10	12	91	23.7	26.7	1.07
5	Fe ₃ O ₄ @aSiO ₂ -click-ZnPTPP	GMA	DDMAT	10	12	95	27.3	34.2	1.12
6	Fe ₃ O ₄ @aSiO ₂ -click-ZnPTPP	NIPAM	DDMAT	10	2	96	22.1	28.7	1.08
7	Fe ₃ O ₄ @aSiO ₂ -click-ZnPTPP	HPMA	DDMAT	10	24	92	26.7	34.1	1.08
8	Fe ₃ O ₄ @aSiO ₂ -click-ZnPTPP	MA	DDMAT	10	6	95	16.7	17.8	1.06
9 ^e	Fe ₃ O ₄ @aSiO ₂ -click-ZnPTPP	<i>n</i> BA	PMA-DDMAT	10	12	92	40.2	47.3	1.14
10 ^e	Fe ₃ O ₄ @aSiO ₂ -click-ZnPTPP	GMA	PMA-DDMAT	10	12	90	42.3	55.5	1.15
11 ^e	Fe ₃ O ₄ @aSiO ₂ -click-ZnPTPP	NIPAM	PMA-DDMAT	10	6	94	37.9	48.6	1.10
12	ZnPTPP	MA	DDMAT	10	12	97	17.1	18.2	1.04
13	ZnPTPP	MA	DDMAT	50	2	96	16.9	18.4	1.06

^a The reactions were performed under green LED light irradiation (5 W, $\lambda_{max} = 520$ nm, 1.3 mW/cm²) in the absence of oxygen at 25 °C in DMSO ([M]₀/[CTA] = 200:1).

^b The molecular weight was calculated using the following equation: $M_{n,NMR} = [M]_0/[CTA] \times MW^M \times \alpha + MW^{CTA}$, where [M]₀, [CTA], MW^M, α and MW^{CTA} correspond to initial monomer concentration, initial CTA concentration, molar mass of monomer, monomer conversion determined from ¹H NMR spectroscopy, and molar mass of CTA.

^c Determined from GPC results (calibration with linear PMMA standards), polydispersity index (\mathcal{D}) = $M_{w,GPC}/M_{n,GPC}$.

^d Abbreviations: PC, photocatalyst; ZnPTPP, 5-(4'-propargyloxyphenyl)-10,15,20-triphenyl-21*H*,23*H*-porphine zinc; MA, methyl acrylate; *n*BA, *n*-butyl acrylate; GMA, glycidyl methacrylate; NIPAM, *N*-isopropylacrylamide; HPMA, *N*-(2-hydroxypropyl) methacrylamide; St, styrene; CTA, chain transfer agent; CPPA, 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid; DDMAT, 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid.

^e The block copolymers were prepared using PMA-DDMAT as macroinitiators in Entry 8.

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